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Mechanisms for the Reactions of OH with Two Unsaturated Aldehydes: Crotonaldehyde and Acrolein

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The mechanisms for the reaction of OH with the unsaturated aldehydes, acrolein and crotonaldehyde, have been determined at 1 atm total pressure in the presence of NO_x using an environmental chamber/FTIR spectrometer system. Products observed in the OH-initiated oxidation of acrolein were CO, CO_2, CH_2O, $HOCH_2CHO$ (glycolaldehyde), and HCOOH, while the major products identified in the OH-initiated oxidation of crotonaldehyde were CO, CO_2, CH_3CHO, and HC(O)CHO (glyoxal). Also observed were two PAN-type species, identified as $CH_2{=}CH{-}C(O)O_2NO_2$ (APAN) from acrolein oxidation and $CH_3{-}CH{=}CH{-}C(O)O_2NO_2$ (CPAN) from crotonaldehyde. The near-complete mass balance obtained in these experiments allows for a quantitative assessment of the branching ratios for abstraction and addition in these reactions. It is shown that about 68% (50%) of the OH reaction with acrolein (crotonaldehyde) proceeds via abstraction of the aldehydic H, with the remainder occurring via addition to the double bond. The data allow for a more accurate assessment of the atmospheric source strength of APAN, a species which has now been identified in ambient air. Trends in the reactivity of acrolein and its methylated derivatives, methacrolein and crotonaldehyde, are also discussed; data are shown to be consistent with structure−reactivity considerations.

Introduction

Unsaturated aldehydes (acrolein, $CH_2{=}CH{-}CHO$, and its methylated derivatives methacrolein, $CH_2{=}C(CH_3){-}CHO$, and crotonaldehyde, $CH_3{-}CH{=}CH{-}CHO$) are present in the atmosphere as the result of direct anthropogenic emissions (e.g., from combustion sources), or as the result of the oxidation of dienes. For example, it is well know that methacrolein is a major first-generation product of isoprene degradation,[1] while acrolein is generated as a byproduct of butadiene oxidation.[2,3]

Due to its central importance in the oxidation of isoprene, a great deal is known about the atmospheric fate of methacrolein.[4−9] The dominant atmospheric loss for this species is via reaction with OH, with photolysis and reaction with O_3 and NO_3 playing at most a minor role. With a value for k_1 of 2.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K,[6] the atmospheric lifetime during the day for this species is ≈2−3 h. It has been shown that the OH reaction occurs 50−55% via addition of OH to the C═C double bond (R1a and R1b), and 45−50% via abstraction of the aldehydic hydrogen (R1c), leading to the formation of three peroxy radicals in the atmosphere:[4,5]

$$OH + CH_2{=}C(CH_3){-}CHO\ (+O_2) \rightarrow HOCH_2{-}C(OO)(CH_3){-}CHO \quad (R1a)$$

$$\rightarrow OOCH_2{-}C(CH_3)(OH){-}CHO \quad (R1b)$$

$$\rightarrow CH_2{=}C(CH_3){-}C(O)O_2 \quad (R1c)$$

Among the suite of products generated from the ensuing chemistry is methacryloylperoxynitrate (MPAN, an unsaturated PAN analogue), which has been identified in ambient air in many continental regions:[10−19]

$$CH_2{=}C(CH_3)C(O)O_2 + NO_2 + M \rightarrow CH_2{=}C(CH_3)C(O)O_2NO_2 + M \quad (R2)$$

In fact, simultaneous measurements of MPAN (believed to be derived from almost exclusively biogenic sources), PPN ($CH_3CH_2C(O)O_2NO_2$, of anthropogenic origin), PAN (of mixed biogenic/ anthropogenic origin), and O_3 have been used to quantify the relative contribution of biogenic and anthropogenic hydrocarbons to ozone production.[13,16] However, the recent finding of a rapid loss of MPAN via reaction with OH[20] calls into question some of the assumptions made in these analyses.

At present, less is known about the mechanism of the reaction of OH with either acrolein or crotonaldehyde:

$$OH + CH_2{=}CH{-}CHO \rightarrow products \quad (R3)$$

$$OH + CH_3{-}CH{=}CH{-}CHO \rightarrow products \quad (R4)$$

Rate coefficients for these reactions are well established,[21−25] $k_3 = 2.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $k_4 = 3.4 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, and some products of the oxidation have been identified and quantified.[3,25,26] In particular, during the course of our investigations, Magneron et al.[25] published data which suggested that ≈20−25% of (R3) occurs via addition pathways, and that both addition and abstraction pathways are operative in (R4). Nonetheless, a complete accounting of the product yields, and hence an accurate assessment of the branching ratio for OH addition and abstraction channels in (R3) and particularly (R4), has yet to be achieved.

Interest in the chemistry of acrolein has been stimulated by the recent observation of acryloylperoxy nitrate ($CH_2{=}CHCOO_2NO_2$, APAN, referred to as vinyl PAN in refs 25 and 26) in ambient air.[27,28] Tanimoto and Akimoto[27] observed this species at both an urban site (suburban Tokyo) and a more

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remote site (Rishiri Island, northern Japan). Roberts et al.[28] have identified APAN in ambient air near Houston, TX as part of the recently completed TEXAS 2000 Air Quality Study. Elevated APAN mixing ratios in this region were attributed in part to large emissions of 1,3-butadiene and/or acrolein from the petrochemical industry.

Interpretation of these APAN data will require knowledge of both its sources (acrolein oxidation) and its sinks (expected to be reaction with OH and thermal decomposition, by analogy to MPAN[20,29]). Regarding the source strength, it is clear that an understanding of the relative contribution of addition and abstraction in the reaction of OH with acrolein is required, since only the abstraction channel (R3c) can lead to APAN production:

$$\mathrm{OH + CH_2{=}CH{-}CHO\ (+O_2)}$$

$$\rightarrow \mathrm{HOCH_2{-}CH(OO){-}CHO} \qquad \text{(R3a)}$$

$$\rightarrow \mathrm{OOCH_2{-}CH(OH){-}CHO} \qquad \text{(R3b)}$$

$$\rightarrow \mathrm{CH_2{=}CH{-}C(O)O_2} \qquad \text{(R3c)}$$

In this study, experiments are conducted in an environmental chamber/FTIR absorption system to determine the end products of the OH-initiated oxidation of both acrolein and crotonaldehyde. These data are interpreted in terms of the branching ratios for reactions (R3a−c), and for the analogous reaction channels occurring in the reaction of OH with crotonaldehyde:

$$\mathrm{OH + CH_3{-}CH{=}CH{-}CHO\ (+O_2)}$$

$$\rightarrow \mathrm{CH_3{-}CH(OH){-}CH(OO){-}CHO} \qquad \text{(R4a)}$$

$$\rightarrow \mathrm{CH_3{-}CH(OO){-}CH(OH){-}CHO} \qquad \text{(R4b)}$$

$$\rightarrow \mathrm{CH_3{-}CH{=}CH{-}C(O)O_2} \qquad \text{(R4c)}$$

Trends in the reactivity of acrolein, methacrolein, and crotonaldehyde are discussed, as are the implications of the results for the atmospheric source of APAN.

Experimental Section

All experiments described here were conducted in a 47 L stainless steel environmental chamber,[20,30] which is interfaced to a Fourier transform infrared spectrometer via a set of Hanst-type multipass optics (observational path length 32.6 m). Spectra were obtained at a resolution of 1 $\mathrm{cm^{-1}}$ from the coaddition of 200 scans (acquisition time 3−4 min), and covered the range 800−3900 $\mathrm{cm^{-1}}$. Photolyses were carried out along the length of the chamber, using the output of a Xe-arc lamp filtered to provide radiation in the range 240−400 nm.

Products of the OH-initiated oxidation of both acrolein and crotonaldehyde were measured at 700−720 Torr total pressure (O_2 partial pressure 150 Torr, balance N_2) from the photolysis of mixtures of an OH precursor (methyl or ethyl nitrite), the unsaturated aldehyde, and NO. Ethyl nitrite was used as the OH source for the acrolein experiments, since methyl nitrite photolysis generates formaldehyde, a likely acrolein oxidation product. For studies of crotonaldehyde, most experiments were carried out using methyl nitrite, to avoid acetaldehyde production from ethyl nitrite. A few experiments were conducted using ethyl nitrite, however, to assess the possibility of CH_2O production from crotonaldehyde oxidation. Typical initial concentrations were as follows: methyl or ethyl nitrite, $(1.5-2.8) \times 10^{15}$ molecule $\mathrm{cm^{-3}}$; acrolein, $(3.5-8) \times 10^{14}$ molecule $\mathrm{cm^{-3}}$ or crotonaldehyde, $(2.4-14) \times 10^{14}$ molecule $\mathrm{cm^{-3}}$; NO, $\approx 3.5 \times 10^{14}$ molecule $\mathrm{cm^{-3}}$. To obtain product yield data, mixtures were photolyzed for four to five periods (each of duration 2−3 min), with an IR spectrum recorded following each irradiation.

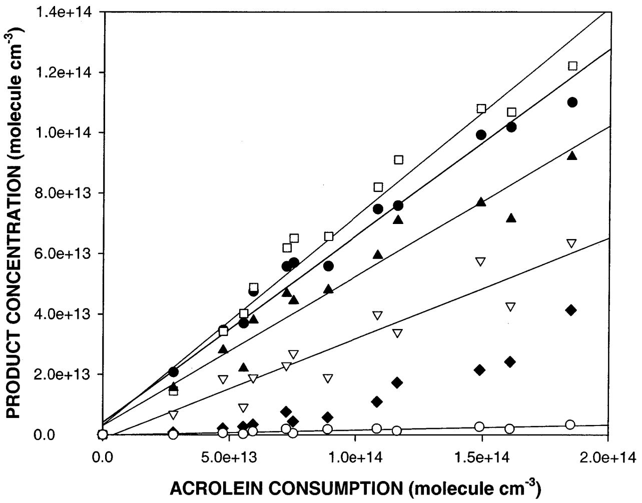

Figure 1. Product concentrations observed from the OH-initiated oxidation of acrolein in 700 Torr of synthetic air, plotted as a function of acrolein consumption. Details of the experimental conditions are given in the text. Open squares, CO_2; filled circles, CO; filled triangles, CH_2O; open triangles, glycolaldehyde; filled diamonds, APAN; open circles, HCOOH.

Some experiments, using Cl-atoms to initiate oxidation, were carried out specifically to determine IR spectra for the unsaturated PAN analogues of MPAN, i.e., APAN from acrolein and CPAN from crotonaldehyde (see results section for details). These experiments were conducted in 1 atm of synthetic air, and involved the photolysis of Cl_2 ($\approx 5 \times 10^{15}$ molecule $\mathrm{cm^{-3}}$) in the presence of either crotonaldehyde or acrolein ($\approx 7 \times 10^{14}$ molecule $\mathrm{cm^{-3}}$) and NO_2 (1.5×10^{14} molecule $\mathrm{cm^{-3}}$).

Quantification of reactants and products was done by comparison with reference spectra recorded with our spectrometer system,[5,31−33] with the exception of the unsaturated PAN species ($\mathrm{CH_2{=}CH{-}C(O)O_2NO_2}$ and $\mathrm{CH_3{-}CH{=}CH{-}C(O)O_2{-}NO_2}$) whose identification and quantification is described in the results section. Quantification was done primarily using the following absorption bands: CO, 2080−2200 $\mathrm{cm^{-1}}$; CO_2, 2300−2380 $\mathrm{cm^{-1}}$; CH_2O, near 1745 $\mathrm{cm^{-1}}$; glycolaldehyde, near 1115 $\mathrm{cm^{-1}}$; glyoxal, near 1730 $\mathrm{cm^{-1}}$ and/or 2835 $\mathrm{cm^{-1}}$; CH_3CHO, 1320−1490 $\mathrm{cm^{-1}}$ and/or 1745 $\mathrm{cm^{-1}}$. Our absorption cross sections for glycolaldehyde are consistent with previous studies.[34,35] Minor corrections (less than 10%) to product yield data were made to account for product loss via reaction with OH.

Chemicals used in this study and their sources and purities were as follows: methyl nitrite and ethyl nitrite, synthesized according to the procedure of Taylor et al.;[36] O_2, UHP, U. S. Welding; N_2, boil-off from liquid N_2, U. S. Welding; acrolein, 90%, Aldrich; crotonaldehyde, 99%, Aldrich; NO, UHP, Linde; Cl_2, HP, Matheson. Gases were used as received. Acrolein and crotonaldehyde were subjected to several freeze−pump−thaw cycles prior to use.

Results and Discussion

Products of Reaction of OH with Acrolein. Products observed following the OH-initiated oxidation of acrolein were CO_2, CO, CH_2O, glycolaldehyde ($HOCH_2CHO$), and formic acid; concentrations of these species, corrected for the occurrence of secondary reactions,[37] as a function of acrolein consumption, are shown in Figure 1. These product concentrations were observed to be linear with acrolein consumption, indicating that all are likely primary products (with the possible

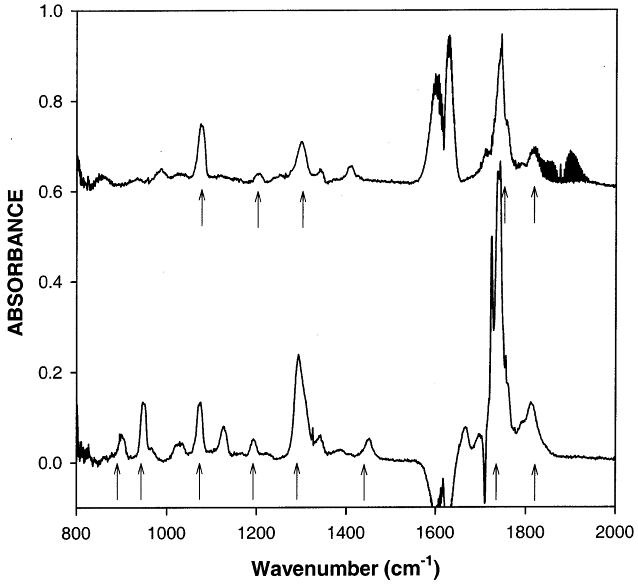

Figure 2. Infrared absorption spectra observed following the photolysis of a mixture of Cl_2 (5 × 10^{15} molecule cm^{-3}), acrolein (upper trace, 7 × 10^{14} molecule cm^{-3}) or crotonaldehyde (lower trace, 7 × 10^{14} molecule cm^{-3}), NO_2 (1.5 × 10^{14} molecule cm^{-3}), O_2 (150 Torr) and N_2 (550 Torr). Absorption features due to the parent aldehyde have been subtracted for clarity. Labeled peaks are assigned to APAN, $CH_2{=}CH{-}C(O)OONO_2$, or CPAN ($CH_2{=}CH{-}C(O)OONO_2$), see text for details.

exception of formic acid, see below). As will be detailed later, concentrations of CO_2, CO, and CH_2O are expected to level off somewhat toward the end of an experiment (due to APAN formation), but this effect is not immediately evident in the data. Product yields, obtained from the slopes of the data shown in Figure 1, are as follows: CO_2, 70 ± 5%; CO, 62 ± 5%; CH_2O, 49 ± 4%; and glycolaldehyde, 32 ± 4%, and formic acid, 1.5 ± 0.7%. The origin of the minor product formic acid is not known, but may be heterogeneous in nature. As its formation at such low levels has no bearing on the data interpretation, it will not be discussed further.

Also observed in the product spectra were absorption features at 1075, 1204, 1298, 1745, and 1820 cm^{-1}. The growth of these features was found to be nonlinear with respect to acrolein consumption, accelerating toward the end of an experiment when NO_2/NO concentration ratios were at a maximum. Since the intensities of these absorption features grew in unison (i.e., their relative intensities remained constant), it is likely that they are all due to a single species (or at least that they are all obtained from the same reaction). On the basis of the position of the absorption bands (note that PAN and MPAN both have absorption features near 1300, 1740, and 1820 cm^{-1})[4,38] and on the basis of the observed temporal profile, we assign these absorption features to the PAN analogue, acryloylperoxynitrate, $CH_2{=}CH{-}C(O)O_2NO_2$ (APAN).

Further confirmation of the identity of the unidentified absorber as APAN was obtained from experiments involving photolysis of Cl_2/acrolein/NO_2/air mixtures. Following a brief photolysis period (30 s), absorption features at 1075, 1204, 1298, 1745, and 1820 cm^{-1} again appeared along with other absorption features at 1304 cm^{-1} and 1725 cm^{-1} due to HO_2NO_2,[39] see Figure 2 (upper trace). Upon sitting in the dark, the features at 1075, 1204, 1298, 1745, and 1820 cm^{-1} remained unchanged, while the HO_2NO_2 features decreased (presumably due to thermal decomposition). As is the case with OH, Cl-atom reaction with acrolein can occur via addition to the double bond, or via abstraction of the aldehydic H atom. In the presence of O_2 and NO_2, APAN is expected to be the sole product obtained from abstraction, while Cl addition under these conditions would generate chlorinated peroxynitrate species, products which obviously will not be formed following OH attack:

TABLE 1: Peak Absorption Cross Sections (10^{-18} cm^2 molecule^{-1}) for PAN,[38] MPAN,[4] APAN, and CPAN (This Work, Assumed by Analogy, See Text for Details)

	PAN	MPAN	CPAN	APAN
794	1.14	1.2		
901			0.22	
950			0.65	
1070		1.6	0.65	1.8
1125			0.3	
1163	1.47			
1193			0.18	
1204				0.34
1300	1.1	1.28	1.1	1.3
1452			0.21	
1740	2.9	3.04	3.2	2.8
1810		0.8	0.6	0.8
1840	1			

$$Cl + CH_2{=}CH{-}CHO\ (+O_2,NO_2)$$

$$\rightarrow ClCH_2{-}CH(OONO_2){-}CHO \qquad (R5a)$$

$$\rightarrow O_2NOOCH_2{-}CHCl{-}CHO \qquad (R5b)$$

$$\rightarrow CH_2{=}CH{-}C(O)O_2NO_2 \qquad (R5c)$$

Thus, it seems reasonable to assume that the absorption features that are common to the Cl- and OH-initiated experiments (1075, 1204, 1298, 1745, and 1820 cm^{-1}) are indeed due to APAN. Furthermore, the observed "dark" behavior is as expected: APAN is stable over the course of an hour or more, while loss of HO_2NO_2 occurs to a significant extent over this time period.

An absolute calibration of the APAN infrared spectrum cannot be done without prior knowledge of the branching ratios for (R5). Instead, an approximate calibration is obtained from an assumption of similar intensities for APAN bands compared to the analogous absorption features in MPAN[4] and PAN.[38] To accomplish this, an average absorption cross section for the 1300 and 1740 cm^{-1} bands was established using the MPAN and PAN data, and the APAN spectrum was adjusted to achieve best agreement with these average absorption cross sections. Use of these absorption cross sections (which are given in Table 1) leads to the conclusion that about 20% of the reaction of Cl with acrolein occurs via abstraction, (R5c). This branching ratio is in quantitative agreement with conclusions drawn from a recently published assessment of Cl-atom reactivity with unsaturated oxygenates,[40] thus lending support to our APAN calibration.

The assumed cross sections can also be used to quantify the APAN yields following reaction of OH with acrolein, as shown in Figure 1. As discussed earlier, these yields vary with the extent of acrolein consumption, reaching a maximum level of 22% at the highest acrolein conversion. Once the contribution of APAN is included, the observed products in the OH-initiated oxidation of acrolein represent on average 97 ± 7% of the reacted carbon, indicating that no major product(s) remain unaccounted for. It now remains to assess these product yields in terms of the branching ratios for (R3a)−(R3c). As pointed out above, reaction of OH with acrolein will result in the generation of three peroxy radicals, $HOCH_2{-}CH(OO){-}CHO$, $OOCH_2{-}CH(OH){-}CHO$, and $CH_2{=}CH{-}C(O)O_2$. Under the conditions of our experiments, the main fate of these species will be reaction with NO to generate the corresponding oxy radicals:

$$\mathrm{HOCH_2{-}CH(OO){-}CHO + NO \rightarrow HOCH_2{-}CH(O){-}CHO + NO_2} \quad \mathrm{(R6)}$$

$$\mathrm{OOCH_2{-}CH(OH){-}CHO + NO \rightarrow OCH_2{-}CH(OH){-}CHO + NO_2} \quad \mathrm{(R7)}$$

$$\mathrm{CH_2{=}CH{-}C(O)O_2 + NO \rightarrow CH_2{=}CH{-}C(O)O + NO_2} \quad \mathrm{(R8)}$$

Organic nitrates are also possible products of these RO_2/NO reactions, though yields are expected[41] to be small, probably <5%. Reaction of the peroxy radicals with NO_2 will also occur,

$$\mathrm{HOCH_2{-}CH(OO){-}CHO + NO_2 \rightarrow HOCH_2{-}CH(OONO_2){-}CHO} \quad \mathrm{(R9)}$$

$$\mathrm{OOCH_2{-}CH(OH){-}CHO + NO_2 \rightarrow O_2NOOCH_2{-}CH(OH){-}CHO} \quad \mathrm{(R10)}$$

$$\mathrm{CH_2{=}CH{-}C(O)O_2 + NO_2 \rightarrow CH_2{=}CH{-}C(O)O_2NO_2\ (APAN)} \quad \mathrm{(R11)}$$

though the peroxynitrates formed in (R9) and (R10) are likely to be thermally unstable at 298 K. On the other hand, APAN formed in (R11) is stable and, as shown above, is a detectable end-product of OH abstraction.

The chemistry of the oxy species generated in (R6) to (R8) can be inferred by analogy to the chemistry of other oxy radicals,[41,42] and more specifically by analogy to chemistry occurring in methacrolein oxidation.[4,5] We will first consider the two oxy radicals formed via OH-addition pathways, $HOCH_2-CH(O)-CHO$ and $OCH_2CH(OH)-CHO$. The $HOCH_2-CH(O)-CHO$ species will decompose, with the most likely end products being glycolaldehyde and CO, with a possible minor channel to form CH_2O and glyoxal:

$$\mathrm{HOCH_2{-}CH(O){-}CHO \rightarrow HOCH_2{-}CHO + HCO} \quad \mathrm{(R12a)}$$

$$\mathrm{\rightarrow CH_2OH + HC(O)CHO} \quad \mathrm{(R12b)}$$

$$\mathrm{HCO + O_2 \rightarrow HO_2 + CO} \quad \mathrm{(R13)}$$

$$\mathrm{CH_2OH + O_2 \rightarrow CH_2O + HO_2} \quad \mathrm{(R14)}$$

The $OCH_2-CH(OH)-CHO$ radical will also be subject to rapid decomposition, yielding formaldehyde and glyoxal:

$$\mathrm{OCH_2{-}CH(OH){-}CHO \rightarrow CH_2O + HOCH{-}CHO} \quad \mathrm{(R15)}$$

$$\mathrm{HOCH{-}CHO + O_2 \rightarrow HC(O)CHO + HO_2} \quad \mathrm{(R16)}$$

To assess the importance of the two addition pathways, we first note that glyoxal was not detected as a reaction product (yield of glyoxal and hence branching ratio to (R3b) ≤ 8%). Furthermore, the lack of significant glyoxal formation indicates that the majority of the $HOCH_2-CH(O)-CHO$ radicals (formed via (R3a), followed by (R6)), must lead to glycolaldehyde. Since glycolaldehyde is not likely to be a product of OH abstraction (see below), and assuming minimal nitrate production in (R6), a branching ratio to (R3a) of ≈32% can be derived. Allowing for a possible 8% glyoxal yield gives an upper limit for the branching ratio to OH addition of $(k_{3a}+k_{3b})/k_3$ of ≤ 44%, with $k_{3a} \geq 4\,k_{3b}$. The larger rate coefficient for external OH addition to acrolein is consistent with findings in the OH/methacrolein reaction, $k_{1a} \geq 5\,k_{1b}$.[4,5]

It now remains to consider the end-products of OH abstraction, (R3c). As shown above, the $CH_2{=}CH-C(O)O_2$ radical generated following (R3c) will either react with NO_2 to form APAN (R11), or with NO to form $CH_2{=}CHC(O)O$, (R8). The $CH_2{=}CHC(O)O$ species is then expected to undergo rapid decomposition to generate CO_2 and the vinyl radical:

$$\mathrm{CH_2{=}CH{-}C(O)O \rightarrow CH_2{=}CH + CO_2} \quad \mathrm{(R17)}$$

Thus, abstraction (R3c) is expected to yield either APAN or (at least one) CO_2, and the sum of the yields of these two species represents an upper limit to the abstraction channel branching ratio, $k_{3c}/k_3 \leq 0.9$. As will be shown below, further CO_2 appears to be generated from the vinyl radical, and hence k_{3c}/k_3 is indeed less than 0.9.

The reaction of vinyl radical with O_2 is known to be rapid, $k_{18} = 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1},[43−47] and thus represents the sole fate of this species under our experimental conditions. Products of this reaction have not been quantitatively determined as yet, however. Gutman and co-workers[44,45] have shown that formation of HCO and CH_2O is important at low pressures, a result recently confirmed by Wang et al.[48] Furthermore, Wang et al.[48] demonstrated the existence of a measurable yield of CH_3 and CO_2, (R18b), at low pressures:

$$\mathrm{CH_2{=}CH + O_2 \rightarrow CH_2O + HCO} \quad \mathrm{(R18a)}$$

$$\mathrm{\rightarrow CH_3 + CO_2} \quad \mathrm{(R18b)}$$

In our system, HCO will be rapidly converted to CO, while CH_3 radicals will be converted to CH_2O:

$$\mathrm{CH_3 + O_2 \rightarrow CH_3O_2} \quad \mathrm{(R19)}$$

$$\mathrm{CH_3O_2 + NO \rightarrow CH_3O + NO_2} \quad \mathrm{(R20)}$$

$$\mathrm{CH_3O + O_2 \rightarrow CH_2O + HO_2} \quad \mathrm{(R21)}$$

At atmospheric pressure, the formation of a stable vinyl peroxy radical may also occur:[49]

$$\mathrm{CH_2{=}CH + O_2 \rightarrow CH_2{=}CHOO} \quad \mathrm{(R18c)}$$

The fate of this species is open to speculation, but may include formation of ketene, glyoxal, or CO and CH_2O.[50,51]

Upon consideration of the data in Figure 1, and taking into account the 32% yield of glycolaldehyde and CO from OH addition channels, it is apparent that the following products are obtained via abstraction: CO_2 (yield ≈70%), CH_2O (≈49%), CO (≈30%), and APAN (≈5−22%, depending on the extent of acrolein conversion). Note that, since the APAN yield increases with extent of conversion, some downward curvature in the yields of CO, CO_2, and CH_2O is likely. Given our observation of essentially 100% carbon balance, it follows that these products represent the sole end-products of abstraction, which must contribute ≈68% to the total reaction. From the discussion given above, it seems likely that three sets of products can be obtained from the abstraction pathway: APAN, via (R11); $CO_2 + CH_2O + CO$, via (R8), (R17), and (R18a); and $2CO_2 + CH_2O$ via (R8), (R17), (R18b), and (R19)−(R21). The yield data are consistent with this supposition. First, a plot of the sum of the concentrations of CO (in excess to that formed

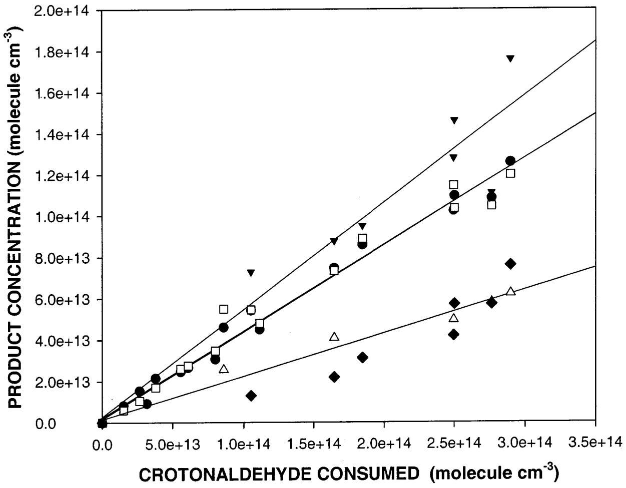

Figure 3. Product concentrations observed from the OH-initiated oxidation of crotonaldehyde in 700 Torr of synthetic air, plotted as a function of crotonaldehyde consumption. Details of the experimental conditions are given in the text. Filled triangles, acetaldehyde; open squares, CO_2; filled circles, CO; open triangles, glyoxal; filled diamonds, CPAN.

in the addition channel), CH_2O, CO_2 and APAN versus acrolein consumption (on a per carbon basis) yielded a slope of 68 ± 8%. Furthermore, a plot of the sum of the concentrations of APAN and CH_2O versus acrolein consumption, on a molar basis, also yielded a slope of 68 ± 8%. Further consideration of the CO and CO_2 data indicate that toward the end of an experiment, the $CO_2 + HCHO + CO$ channel was occurring with about a 30% yield, the $2CO_2 + CH_2O$ channel with about a 20% yield, and the APAN channel with about a 20% yield. Thus, it appears likely that pathways (R18a) and (R18b) are both occurring in the vinyl + O_2 reaction, consistent with the findings of Wang et al.[48] However, yields of CO_2 are higher relative to CO than might be expected if the $CH_3 + CO_2$ channel (R18b) is minor, and may indicate that other sources of CO_2 are present in our experiments which skew our determination of the relative importance of (R18a) and (R18b).

Previous studies of the reaction of OH with acrolein have been carried out by Grosjean et al.,[26] Liu et al.[3] and, very recently, by Magneron et al.[25] Grosjean et al. identified APAN (referred to as vinyl PAN in their paper), CH_2O, and glycolaldehyde and/or glyoxal as products, though no yield data were reported. Similarly, Liu et al. reported the formation of CH_2O, glyoxal, glycolaldehyde, glycidaldehyde, malonaldehyde, and 3-hydroxy-propanal following reaction of OH with acrolein; again, no yield data were reported. Magneron et al.[25] identified glyoxal (yield 5–10%), glycolaldehyde (12–25%), ketene (2–3%), as well as APAN, CH_2O, and CO (no yield data given) as products of (R3). Where comparisons are possible, the yields reported by Magneron et al.[25] are in agreement with our data, within the combined uncertainties. On the basis of their combined glycolaldehyde and glyoxal yields,[25] these workers suggested a ≈25% occurrence of addition pathways in (R3), similar to our conclusion.

Products of Reaction of OH with Crotonaldehyde. Products observed following the OH-initiated oxidation of crotonaldehyde were CO (42 ± 4% yield), CO_2 (41 ± 4%), glyoxal (21 ± 5%), and acetaldehyde (51 ± 9%), see Figure 3. Some formaldehyde may also be formed, yield <12%. Uncertainties in the crotonaldehyde study are larger than in the case of acrolein, owing to the more complex nature of the IR spectra involved.

After accounting for the products listed above, a number of additional unassigned absorption features (901, 950, 1070, 1193, 1300, 1452, 1740, and 1820 cm^{-1}) were apparent in the product spectra. As was the case for the absorption bands attributed to APAN, the appearance profile of these features was nonlinear with crotonaldehyde consumption, accelerating toward the end of an experiment. Furthermore, these same absorption features were evident (with the same relative intensities) following the photolysis of mixtures of Cl_2, crotonaldehyde, and NO_2 in air, see Figure 2 (lower trace). Using the same logic applied above for APAN, it seems reasonable to assign these absorption features to a crotonaldehyde-derived unsaturated PAN species, $CH_3-CH{=}CH-C(O)O_2NO_2$, hereafter referred to as CPAN. As was the case for APAN, an absolute calibration of the CPAN infrared spectrum is not possible without prior knowledge of the mechanism for reaction of Cl with crotonaldehyde. However, approximate absorption cross sections can be obtained from an assumption of similar band strengths for absorption features common to PAN, MPAN, APAN, and CPAN. Absorption cross sections assigned to the various CPAN absorption features (obtained using the same logic as was use for APAN spectral calibration discussed earlier) are given in Table 1, and CPAN concentrations observed in the OH-initiated crotonaldehyde oxidation experiments are shown in Figure 3. The identified products (CO, CO_2, CH_3CHO, glyoxal, and CPAN) account for, on average, 77 ± 12% of the reacted crotonaldehyde carbon, indicating the likelihood of the existence of an additional undetected product.

The chemistry pursuant to reaction of OH with crotonaldehyde, (R4a)–(R4c),

$$\mathrm{OH + CH_3{-}CH{=}CH{-}CHO\ (+O_2)}$$

$$\rightarrow \mathrm{CH_3{-}CH(OH){-}CH(OO){-}CHO} \tag{R4a}$$

$$\rightarrow \mathrm{CH_3{-}CH(OO){-}CH(OH){-}CHO} \tag{R4b}$$

$$\rightarrow \mathrm{CH_3{-}CH{=}CH{-}C(O)O_2} \tag{R4c}$$

is expected to be similar to that observed in the case of acrolein. Peroxy radicals generated by OH addition, (R4a) and (R4b), will be converted predominantly to the corresponding oxy radicals, whose subsequent fate will be decomposition to form either glyoxal and acetaldehyde or CO and 2-hydroxypropanal, $CH_3CH(OH)CHO$:

$$\mathrm{CH_3{-}CH(OH){-}CH(OO){-}CHO + NO} \rightarrow \mathrm{CH_3{-}CH(OH){-}CH(O){-}CHO + NO_2} \tag{R22}$$

$$\mathrm{CH_3{-}CH(OO){-}CH(OH){-}CHO + NO} \rightarrow \mathrm{CH_3{-}CH(O){-}CH(OH){-}CHO + NO_2} \tag{R23}$$

$$\mathrm{CH_3{-}CH(OH){-}CH(O){-}CHO}$$

$$\rightarrow \mathrm{HCO + CH_3{-}CH(OH)CHO} \tag{R24a}$$

$$\rightarrow \mathrm{CH_3CHOH + HCOCHO} \tag{R24b}$$

$$\mathrm{HCO + O_2} \rightarrow \mathrm{CO + HO_2} \tag{R13}$$

$$\mathrm{CH_3CHOH + O_2} \rightarrow \mathrm{CH_3CHO + HO_2} \tag{R25}$$

$$\mathrm{CH_3{-}CH(O){-}CH(OH){-}CHO} \rightarrow \mathrm{CH_3CHO + CH(OH){-}CHO} \tag{R26}$$

$$\mathrm{CH(OH){-}CHO + O_2} \rightarrow \mathrm{HCOCHO + HO_2} \tag{R27}$$

By analogy to acrolein (see above) and methacrolein,[4,5] products likely to arise from OH abstraction, (R4c), include CPAN:

$$CH_3{-}CH{=}CH{-}C(O)O_2 + NO_2 \rightarrow CH_3{-}CH{=}CH{-}C(O)O_2NO_2 \text{ (CPAN)} \quad (R28)$$

or CO_2 and (via 2-methyl vinyl radical formation) either methyglyoxal, acetaldehyde, methyl ketene, CO, or additional CO_2:

$$CH_3{-}CH{=}CH{-}C(O)O_2 + NO \rightarrow CH_3{-}CH{=}CH{-}C(OO) + NO_2 \quad (R29)$$

$$CH_3{-}CH{=}CH{-}C(OO) \rightarrow CH_3{-}CH{=}CH + CO_2 \quad (R30)$$

$$CH_3{-}CH{=}CH + O_2 \rightarrow CH_3CHO + HCO \quad (R31a)$$

$$\rightarrow CH_3CH_2 + CO_2 \text{ ?} \quad (R31b)$$

$$\rightarrow \text{other products ?} \quad (R31c)$$

$$CH_3CH_2 + O_2 \rightarrow CH_3CH_2O_2 \quad (R32)$$

$$CH_3CH_2O_2 + NO \rightarrow CH_3CH_2O + NO_2 \quad (R33)$$

$$CH_3CH_2O + O_2 \rightarrow CH_3CHO + HO_2 \quad (R34)$$

As mentioned above, the identified products only account for about 77% of the oxidized crotonaldehyde (on a per carbon basis). From a consideration of the chemistry just presented, the most likely candidate for the missing product is 2-hydroxypropanal, $CH_3CH(OH)CHO$. Given the lack of a full carbon balance, determination of the branching ratios for addition and abstraction is not as clear-cut as was the case for acrolein. Nonetheless, a reasonable estimate is attainable. Glyoxal appears to be a product unique to addition, thus providing a lower limit of 21% to addition channels. The sum of the CO_2 and CPAN yields, provides an upper limit (≤64%) to abstraction, see (R28)−(R30). We also note that the acetaldehyde yield (51%) exceeds that of glyoxal (21%). Thus, a significant amount of acetaldehyde must be derived from OH abstraction. In fact, if (R31a) and (R31b) represent the major channels in the reaction of 2-methylvinyl with O_2, as was the case for reaction of vinyl with O_2, the sum of the CPAN yield and "excess" acetaldehyde yield (i.e., the yield of acetaldehyde in excess of its addition coproduct, glyoxal) would provide a measure of the abstraction branching ratio; this term results in a best estimate for the branching to abstraction, k_{4c}/k_4, of ≈50%. Furthermore, from mass balance arguments, the yield of 2-hydroxypropanal cannot exceed a value of 35%. This assumption, coupled with the measured yield of glyoxal (21%), provides an upper limit of about 56% for addition channels. Finally, if it is assumed that the majority of the missing carbon in our product distribution is indeed attributable to 2-hydroxypropanal, the following product channel yields are most consistent with our data toward the end of a run: acetaldehyde and glyoxal via addition, 21%; 2-hydroxypropanal and CO via addition, 35%; CPAN via abstraction, about 20%; CO + CO_2 + acetaldehyde via addition, 7%; 2 CO_2 + acetaldehyde via addition, 19%. While the conclusions drawn here clearly involve some speculation, it seems unlikely that the branching ratios for abstraction and addition are significantly different from each other.

Some products of the OH-initiated oxidation of crotonaldehyde have recently been quantified by Magneron et al.[25] Their yield of glyoxal, 16%, is in agreement with ours, while their yield of acetaldehyde (30 ± 5%) is somewhat lower than ours (note that quantification of acetaldehyde in our spectra is extremely difficult). Other products reported, but for which yield data are not given, include CO, CPAN (referred to as methyl vinyl PAN), formaldehyde, and either methylglyoxal or 2-hydroxypropanal. Though they presented evidence for the occurrence of both abstraction and addition, quantification of the branching ratios to the competing pathways was not possible.

TABLE 2: Total Rate Coefficients and Rate Coefficients for Addition and Abstraction in the Reactions of OH with Unsaturated Aldehydes: All Rate Coefficient Data in Units of 10^{-12} cm^3 molecule^{-1} s^{-1}

compound	total k	% addition	k_{abs}	$k_{addition}$
acrolein	20	32 ± 5	14 ± 2	6 ± 1
methacrolein	28	55 ± 5	13 ± 2	15 ± 2
crotonaldehyde	34	50 ± 15	17 ± 5	17 ± 5

Trends in Reactivity of OH with the Unsaturated Aldehydes. As mentioned in the Introduction, the rate coefficients for reaction of OH with acrolein, methacrolein, and crotonaldehyde are well-known. With these total rate coefficient data, the branching ratio data for acrolein and crotonaldehyde presented above, and previously published data on methacrolein branching ratios,[4,5] it becomes possible to calculate site-specific rate coefficients for abstraction and addition, as is done in Table 2. Inspection of the data shows that the rate coefficients for abstraction from acrolein, methacrolein, and crotonaldehyde are very similar to one another, and are quite similar to the rate coefficient for reaction of OH with acetaldehyde,[52] $k = 1.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. On the other hand, the rate coefficient for OH addition to acrolein (6×10^{-12} cm^3 molecule^{-1} s^{-1}), is considerably smaller than the rate coefficients for the addition of OH to the methyl-substituted species (about 1.6×10^{-11} cm^3 molecule^{-1} s^{-1}). Thus, as expected from structure−reactivity considerations,[53,54] the presence of a methyl group leads to a large enhancement of the reactivity of the double bond (by a factor of 2.5 or so).

As has been presented previously,[53,54] the presence of the adjacent carbonyl group provides a deactivating effect on the reactivity of the double bond toward OH. Note that addition of OH to acrolein (methacrolein or crotonaldehyde) is slower than addition of OH to the corresponding "parent" alkene, propene (2-methyl-propene or 2-butene). In the structure−reactivity framework of Kwok and Atkinson,[54] the −CHO group is assigned a substituent factor of 0.34 relative to a methyl group (that is, the rate coefficient for addition of OH to acrolein is expected to be one-third that of OH addition to propene). Consideration of the data in Table 2 suggests a modest decrease in this parameter, to 0.27.

Finally, it is interesting to speculate upon the actual site of OH addition (i.e., adjacent (α) to the carbonyl group or on the double-bonded carbon furthest from the carbonyl group (*β*)) for the three unsaturated aldehydes. For methacrolein, the large yield of hydroxyacetone (about 45%)[4,5] out of a total of 55% of the reaction occurring via addition, indicates that at least 80% of the addition occurs at the *β*-carbon. Similarly, the large yield of glycolaldehyde (32%) relative to that of glyoxal (<8%) following addition of OH to acrolein again indicates at least 80% OH addition to the (terminal) *β*−carbon. The situation is less clear in the case of crotonaldehyde. However, the upper limit to the yield of 2-hydroxypropanal (35%, see above) coupled with a 20% yield of glyoxal may be an indication of measurable (about 40%) addition occurring at the α-carbon (i.e., adjacent to the carbonyl group), possibly a consequence of the stabilization of the resulting hydroxyalkyl radical by the methyl group in crotonaldehyde. Alternatively, the glyoxal (and coproduct acetaldehyde) may result from (R24b), decomposition of the $CH_3-CH(OH)-CH(O)-CHO$ radical to CH_3CHOH and glyoxal. This reaction may be more favorable than the analogous processes in the oxidation schemes of acrolein, (R12b), or methacrolein,

$$HOCH_2-C(CH_3)(O)-CHO \rightarrow CH_2OH + CH_3C(O)CHO \qquad \text{(R35)}$$

because of the nature of the leaving groups involved (CH_3CHOH in the case of crotonaldehyde, CH_2OH in the acrolein and methacrolein case). Theoretical calculations would be useful in resolving this issue.

Atmospheric Speculation

The atmospheric fate and impact of both acrolein and crotonaldehyde have been discussed in the recent paper by Magneron et al.[25] Reaction with OH is the dominant tropospheric loss process for both species (lifetime a few hrs. for typical daytime $[OH] = (2-3) \times 10^6$ molecule cm^{-3}), with photolysis and reaction with either ozone or NO_3 expected to play only a minor role. The suite of oxygenated products generated in the OH-initiated oxidations of the unsaturated aldehydes (formaldehyde and glycolaldehyde from acrolein, and glyoxal, acetaldehyde, and 2-hydroxypropanal from crotonaldehyde) are all expected to be reasonably short-lived as well,[25,31,32,34,52] as reaction with OH and/or photolysis present efficient removal processes for these species. Lifetimes ranging from a few hours for acetaldehyde to less than 1 h for glyoxal are likely. Thus, these oxygenates will contribute to ozone and HO_x production close to the acrolein/crotonaldehyde source region.

The branching ratio data for reaction of OH with acrolein and crotonaldehyde presented herein provide key information required to assess the source strength of the unsaturated PAN-analogues (APAN and CPAN). Our data show that the acyl peroxy radical, $CH_2{=}CH-C(O)O_2$, will be generated with about 70% yield from the OH/acrolein reaction, while the corresponding $CH_3-CH{=}CH-C(O)O_2$ radical will be generated in about 50% yield from reaction of OH with crotonaldehyde. Formation of APAN (or CPAN) will also be controlled by the relative rate coefficients for (R11) and (R8) (or (R28) and (R29)), expected to be about 0.5 by analogy to the acetylperoxy radical,[52] as well as by the ambient $[NO_2]/[NO]$ ratio, typically 2−8 in the continental boundary layer. By analogy to MPAN,[20,29] OH reaction and thermal decomposition are likely to be the major loss processes for APAN and CPAN. Since the $-C(O)O_2NO_2$ group does not appear to be strongly deactivating,[20] rate coefficients with OH on the order of $(1-2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for APAN, and $(3-4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for CPAN are likely.

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References and Notes

(1) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1990**, *22*, 1221.

(2) Tuazon, E. C.; Alvarado, A.; Aschmann, S. M.; Atkinson, R.; Arey, J. *Environ. Sci. Technol.* **1999**, *33*, 3586.

(3) Liu, X.; Jeffries, H. E.; Sexton, K. G. *Atmos. Environ.* **1999**, *33*, 3005.

(4) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1990**, *22*, 591.

(5) Orlando, J. J.; Tyndall, G. S.; Paulson, S. E. *Geophys. Res. Lett.* **1999**, *26*, 2191.

(6) Gierczak, T.; Burkholder, J. B.; Talukdar, R. K.; Mellouki, A.; Barone, S. B.; Ravishankara, A. R. *J. Photochem. Photobiol. A* **1997**, *110*, 1.

(7) Canosa-Mas, C. E.; Carr, S.; King, M. D.; Shallcross, D. E.; Thompson, K. C.; Wayne, R. P. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4195.

(8) Kwok, E. S. C.; Aschmann, S. M.; Arey, J.; Atkinson, R. *Int. J. Chem. Kinet.* **1996**, *28*, 925.

(9) Carter, W. P. L.; Atkinson, R. *Int. J. Chem. Kinet*. **1996**, *28*, 497.

(10) Bertman, S. B.; Roberts, J. M. *Geophys. Res. Lett.* **1991**, ***18***, 1461.

(11) Grosjean, D.,; Williams, E. L., II; Grosjean, E. *Environ. Sci. Technol*. **1993**, *27*, 110.

(12) Williams, E. L., II; Grosjean, E.; Grosjean, D. J. *Air Waste Manage. Assoc.* **1993**, *43*, 873.

(13) Williams, J.; Roberts, J. M.; Fehsenfeld, F. C.; Bertman, S. B.; Buhr, M. P.; Goldan, P. D.; Hübler, G.; Kuster, W. C.; Ryerson, T. B.; Trainer, M.; Young, V. *Geophys. Res. Lett.* **1997**, *24*, 1099.

(14) Williams, J.; Roberts, J. M.; Bertman, S. B.; Stroud, C. A.; Fehsenfeld, F. C.; Baumann, K.; Buhr, M. P.; Knapp, K.; Murphy, P. C.; Nowick, M.; Williams, E. J. *J. Geophys. Res.* **2000**, *105*, 28943.

(15) Nouaime, G.; Bertman, S. B.; Seaver, C.; Elyea, D.; Huang, H.; Shepson, P. B.; Starn, T. K.; Riemer, D. D.; Zika, R. G.; Olszyna, K. *J. Geophys. Res.* **1998**, *103*, 22463.

(16) Roberts, J. M.; Williams, J.; Baumann, K.; Buhr, M. P.; Goldan, P. D.; Holloway, J.; Hübler, G.; Kuster, W. C.; McKeen, S. A.; Ryerson, T. B.; Trainer, M.; Willliams, E. J.; Fehsenfeld, F. C.; Bertman, S. B.; Nouaime, G.; Seaver, C.; Grodzinsky, G.; Rodgers, M.; Young, V. L. *J. Geophys. Res.* **1998**, *103*, 22473.

(17) Starn, T. K.; Shepson, P. B.; Bertman, S. B.; White, J. S.; Splawn, B. G.; Riemer, D. D.; Zika, R. G.; Olszyna, K. *J. Geophys. Res.* **1998**, *103*, 22425.

(18) Starn, T. K.; Shepson, P. B.; Bertman, S. B.; Riemer, D. D.; Zika, R. G.; Olszyna, K. *J. Geophys. Res.* **1998**, *103*, 22437.

(19) Hansel, A.; Wisthaler, A. *Geophys. Res. Lett.* **2000**, *27*, 895.

(20) Orlando, J. J.; Tyndall, G. S.; Bertman, S. B.; Chen, W.; Burkholder, J. B. *Atmos. Environ.* **2002**, *36*, 1895.

(21) Maldotti, A.; Chiorboli, C.; Bignozzi, C. A.; Bartocci, C.; Carassiti, V. *Int. J. Chem. Kinet.* **1980**, *12*, 905.

(22) Kerr, J. A.; Sheppard, D. W. *Environ. Sci. Technol*. **1981**, *15*, 960.

(23) Atkinson, R.; Aschmann, S. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1983**, *15*, 75.

(24) Edney, E. O.; Kleindienst, T. E.; Corse, E. W. *Int. J. Chem. Kinet.* **1986**, *18*, 1355.

(25) Magneron, I.; Thévenet, R.; Mellouki, A.; Le Bras, G.; Moortgat, G. K.; Wirtz, K. *J. Phys. Chem. A* **2002**, *106*, 2526.

(26) Grosjean, E.; Williams, E. L., II; Grosjean, D. *Sci. Total Environ*. **1994**, *153*, 195.

(27) Tanimoto, H.; Akimoto, H. *Geophys. Res. Lett.* **2001**, *28*, 2831.

(28) Roberts, J. M.; Flocke, F.; Weinheimer, A.; Tanimoto, H.; Jobson, B. T.; Riemer, D.; Apel, E.; Atlas, E.; Donnelly, S.; Stroud, V.; Johnston, K.; Weaver, R.; Fehsenfeld, F. C. *Geophys. Res. Lett.* **2001**, *28*, 4195.

(29) Roberts, J. M.; Bertman, S. B. *Int. J. Chem. Kinet*. **1992**, *24*, 297.

(30) Shetter, R. E.; Davidson, J. A.; Cantrell, C. A.; Calvert, J. G. *Rev. Sci. Instrum.* **1987**, *58*, 1427.

(31) Bacher, C.; Tyndall, G. S.; Orlando, J. J. *J. Atmos. Chem.* **2001**, *39*, 171.

(32) Orlando, J. J., Tyndall, G. S. *Int. J. Chem. Kinet.* **2001**, *33*, 149.

(33) Orlando, J. J.; Tyndall, G. S.; Ceazan, N. *J. Phys. Chem. A* **2001**, *105*, 3564.

(34) Niki, H.; Maker, P. D.; Savage, C. M.; Hurley, M. D. *J. Phys. Chem*. **1987**, *91*, 2174.

(35) Tuazon, E. C.; Atkinson, R. *Int. J. Chem. Kinet.* **1989**, *21*, 1141.

(36) Taylor, W. D.; Allston, T. D.; Moscato, M. J.; Fazekas, G. B.; Kozlowski, R.; Takacs, G. A. *Int. J. Chem. Kinet*. **1980**, *12*, 231.

(37) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.

(38) Tsalkani, N.; Toupance, G. *Atmos. Environ.* **1989**, *23*, 1849.

(39) Graham, R. A.; Winer, A. M.; Pitts Jr., J. N. *Geophys. Res. Lett.* **1978**, *5*, 909.

(40) Wang, W.; Ezell, M. J.; Ezell, A. A.; Soskin, G.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys*., **2002**, *4*, 1824.

(41) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215.

(42) Atkinson, R. *Int. J. Chem. Kinet*. **1997**, *29*, 99.

(43) Fahr, A.; Laufer, A. H. *J. Phys. Chem.* **1988**, *92*, 7229.

(44) Park, J.-Y.; Heaven, M. C., Gutman, D. *Chem. Phys. Lett.* **1984**, *104*, 469.

(45) Slagle, I. R.; Park, J.-Y.; Heaven, M. C.; Gutman, D. *J. Am. Chem. Soc.* **1984**, *106*, 4356.

(46) Krueger, H. Weitz, E., *J. Chem. Phys*. **1988**, *88*, 1608.

(47) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem*. **1995**, *99*, 2247.

(48) Wang, H., Wang, B.; He, Y.; Kong, F. *J. Chem. Phys.* **2001**, *115*, 1742.

(49) Fahr, A.; Laufer, A. H.; Krauss, M.; Osman, R. *J. Phys. Chem*. **1997**, *101*, 4879.

(50) Gutman, D.; Nelson, H. H. *J. Phys. Chem*. **1985**, *89*, 3902.

(51) Zhu, L.; Johnston, G. *J. Phys. Chem.* **1995**, *99*, 15114.

(52) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1999**, *28*, 191.

(53) Atkinson, R. *Int. J. Chem. Kinet*. **1987** *19*, 799.

(54) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.